THE INDEX OF REFRACTION OF CERUSSITE FOR X-RAYS

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE UNIVERSITY OF MICHIGAN

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The Index of Refraction of Cerussite for X-Rays

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The refractive index of cerussite ($PbCO_3$) has been measured for some fourteen wave-lengths lying in the spectral regions from 2500 to 3600 X.U. and from 4800 to 5400 X.U. In this neighborhood are found also the five M absorption limits of lead. On account of the high density (6.6 g per cc) of cerussite, the unit decrement $\delta(=1-\mu)$ is much larger than that of such crystals as calcite, quartz, etc. From the theory of dispersion δ/λ^2 should decrease considerably in the vicinity of the absorption limits. A general decrease in the value of δ/λ^2 was found, especially toward the higher wave-lengths, but it is not evident that there is a very large change in the immediate vicinity of an absorption edge. The method used differs somewhat from those previously employed.

INTRODUCTION

PERHAPS the chief difficulty in determining the index of refraction for x-rays is due to the very small deviation of the beam in passing from one medium to another, even when the glancing angle is small. Several different methods have been used in the past to measure the index for various substances. Among the methods used is one proposed by Bergen Davis and used by von Nardroff,[1] Larsson[2] and others. The essential principle of this method consists in increasing the deviation of a refracted ray of a certain wave-length by reflecting it from a crystal in such a manner that the ray enters or leaves the crystal at a very small angle with the crystal face, instead of at the regular angle given by the Bragg law of reflection. With the exception of von Nardroff's work on iron pyrites (density about 5 g per cc) most of the measurements made by this method, as well as by the method of direct transmission of a ray through a prism of the material, have been for lighter materials such as calcite, quartz, glass, etc. The advantage with lighter materials is, of course, that the absorption is much less—a very important consideration for the longer wave-lengths. For the method of total reflection the absorption is not so serious, but for the elements of higher atomic number the critical angle at which total reflection occurs becomes very indefinite.[3]

The present work takes advantage of the principle suggested by Bergen Davis, but with this difference; instead of artificially preparing a face on a crystal at a certain angle with the atomic planes, a natural face (in this paper referred to as the bevel face) was used, while the spectrum was formed from planes parallel to the other natural face, here called the Bragg face.

Crystals of cerussite ($PbCO_3$) often possess such natural faces making suitable angles with each other, while at the same time the substance is very dense (6.6 g per cc), so that a relatively large value of the unit decrement $(1-\mu)$ is obtained. The faces used were such that the wave-lengths having suitable angles of reflection lie in the portion of the spectrum containing the M absorption edges of lead. Anomalous refraction near the absorption limits has been investigated extensively by Larsson,[2] whose work dealt with the K edges. It was hoped that some similar effect could be observed near the M edges of lead.

The same substance, $PbCO_3$, has been investigated by Hoyt and Lindsay[4] by a somewhat different procedure. In the latter work a single beam was reflected from two faces of the crystal at once, while the present method determines the position of the ray refracted from the bevel face of the crystal by measuring its distance from a reference line reflected from the Bragg face of the same crystal. When both the reference line and the line whose refraction is being investigated are reflected from the Bragg face their separation is the normal one, each line, of course, being displaced slightly by refraction as all lines are in ordinary reflection. Now, if the crystal is turned so that the reference line is still reflected from the Bragg face, while the other is reflected from the bevel face, the separation of the two lines is changed, since the deviation of the ray issuing

[1] R. von Nardroff, Phys. Rev. **24**, 143 (1934).
[2] A. Larsson, Dissertation, Upsala (1929).
[3] E. Nahring, Physik. Zeits. **31**, 799 (1930).
[4] H. C. Hoyt and Geo. A. Lindsay, Phys. Rev. **49**, 498 (1936).

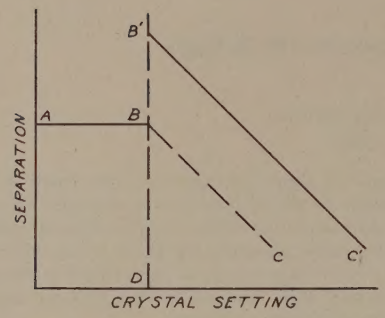

FIG. 1. Separation between reference line and refracted line as crystal is turned.

from the bevel face has been greatly increased. If now we plot the separation between the two lines as measured on the photographic plate, as a function of the angular setting of the crystal, we find a constant separation as long as the two lines are reflected from the Bragg face, but as soon as one line passes to the bevel face there is a sudden change in separation as shown by BB' in Fig. 1. As the crystal is turned further the position of the line from the bevel face changes uniformly because it is no longer reflected from atomic planes passing through the axis of rotation of the spectrograph. Since the angle between the two faces is accurately known, however, the slope of the portion of the line $B'C'$, expressed as the number of millimeters per minute of arc by which the line coming from the bevel face is displaced, simply due to rotation of the crystal, and not at all due to refraction, is given by

$$\frac{\Delta s}{\text{min.}} = \frac{0.104 \sin \alpha \cos \theta}{\sin (\alpha+\theta)} \text{mm/min.} \qquad (1)$$

The angles α and θ are shown in Fig. 2. The numerical factor 0.104 is two times the arc, expressed in mm, which is subtended at a distance equal to the radius of the spectrograph by an angle of one minute.

The line of intersection of the two crystal faces should be placed accurately in the axis of the spectrometer, and no line should be reflected from so near the intersection that it becomes unsymmetrical, for in such a case the measurement of its middle point would be in error.

It becomes necessary to locate with some accuracy the setting of the crystal such that the center of the line falls on the intersection of the two faces. This setting was calculated by taking a continuous spectrum from the Bragg face, with the line to be refracted a short distance from the sharp limit where the continuous spectrum is terminated by the junction between the two faces. From the distance between the line and the termination of the continuous spectrum it is easy to calculate how much more the crystal should be turned to bring the line exactly at the junction of the two faces. This calculation at once gives the point D (Fig. 1).

APPARATUS

The photographs were taken with a Siegbahn vacuum spectrometer of radius 179.2 mm. The slit was 0.035 mm wide. An important feature of the method is that the only special apparatus needed was a crystal holder capable of being tipped about two axes at right angles to each other and also capable of being displaced parallel to these axes. By means of this table the crystal was set so that the line of intersection of the faces remained fixed in position as the crystal was rotated. Thus the line of intersection of the faces was made coincident with the axis of the spectrometer. Suitable spectrum lines were obtained by placing various substances on the anode of the x-ray tube.

GEOMETRY OF THE CRYSTAL USED

Cerussite is orthorhombic in form. Its density is 6.6 g per cc.[5] The axial ratios as determined by the authors and by Hoyt[4] are

$$a : b : c = 0.6102 : 1 : 0.7229.$$

These ratios were obtained by measurement of the grating spaces of several faces of the crystal

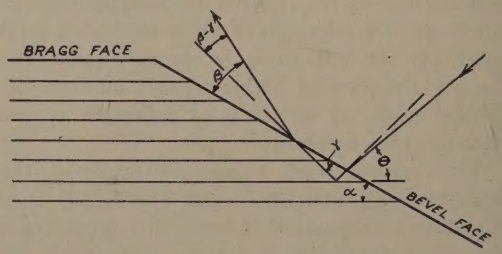

FIG. 2. Reflection and refraction of a ray at a bevel face of the crystal.

[5] *International Critical Tables.*

used, and they agree very well with values given in crystallographic tables. In all, sixteen different determinations of δ were made. For these the (001) face of cerussite was used as the Bragg face six times, the (110) face six times, the (100) face twice, and the (130) face twice. The angle between the Bragg face and the bevel face must be known rather accurately because δ is proportional to the tangent of the angle β, which is the difference between the Bragg angle θ and this angle α between the two faces (see Fig. 2). Since β was only of the order of 2° or 3°, it is evident that α should be known to about 1′. The angle α was measured optically with a spectrometer and found to be as follows. Between faces (110) and (100), 31° 23′ 30″; (110) and (130), 29° 58′ 30″; (001) and (102), 30° 37′ 0″. The face (102) was not used as a Bragg face. The values of the grating space d as measured by a precision method for the remaining four faces denoted above were determined to be as follows.

Face	(110)	(100)	(130)	(001),
d in X.U.	4416	2586	2480	3065.

Formulas for the Calculation of the Index

In Fig. 2 a monochromatic ray is shown entering the bevel face at nearly normal incidence

Table I. *Data for Ca $K\alpha_1$ line. Reference line: Ni $K\alpha_1$ (2nd order). Bragg face (001), (d=3065 X.U.); bevel face, (102); angle α between the faces = 30°−37′−00″; angle θ for Ca $K\alpha_1$ = 33°−09′−09″; angle $\beta=(\theta-\alpha)$ = 2°−03′−09″; slope of $B'C'$ = 0.0494 mm/min.; r = 179.2 mm.*

Plate number	Crystal setting	Separation (mm) Ca $K\alpha_1$ − Ni $K\alpha_1$	
262	274°–28′	3.030	
256′	30′	3.020	
256	30′	3.025	
263	32′	3.035	
264	40′	3.025	
		3.027 mean	
		Ca $K\alpha_1$ − Edge of cont. spec.	
256′	30′	2.453	
256	30′	2.428	
	53.4′	setting for Ca $K\alpha_1$ incident on crystal edge.	
		Ca $K\alpha_1$ − Ni $K\alpha_1$	BB' (mm)
260	58′	3.085	0.285
257	275–00′	2.970	.269
258	02′	2.890	.288
259	04′	2.780	.277
261	06′	2.675	.271
			0.278 mean

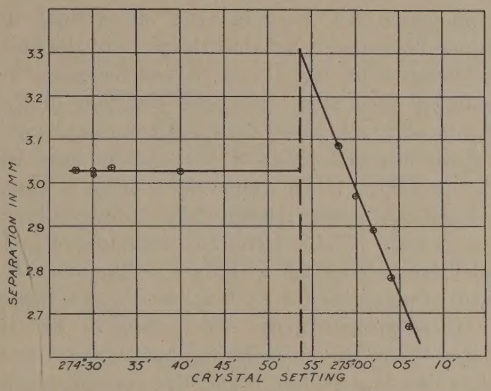

Fig. 3. Separation between Ca $K\alpha_1$ and Ni $K\alpha_1$ as reference line.

and emerging at a very small grazing angle γ inside the crystal, β outside, so that $\beta-\gamma$ is the deviation of this ray on emerging from the crystal. Hence we have

$$\mu = 1-\delta = \cos\beta/\cos\gamma, \tag{2}$$

$$\delta = \frac{\cos\gamma-\cos\beta}{\cos\gamma} = \frac{2\sin\tfrac{1}{2}(\beta+\gamma)\sin\tfrac{1}{2}(\beta-\gamma)}{\cos\gamma}. \tag{3}$$

Since $\beta-\gamma$ is small, $\tfrac{1}{2}(\beta+\gamma)=\gamma$ nearly, and $\sin\tfrac{1}{2}(\beta-\gamma)$ may be put equal to $\tfrac{1}{2}(\beta-\gamma)$.

$$\therefore \quad \delta = (\beta-\gamma)\tan\beta. \tag{4}$$

Referring to Fig. 1, BB'/r, where r is the radius of the spectrograph, should be the angle by which the ray is deviated by refraction on emerging from the bevel face. It is necessary, however, to add to this angle a small amount, because of the refraction of the ray from the Bragg face, for BB' is only the *change* in the displacement when the ray passes from the Bragg face to the bevel face. We may write, then

$$\beta-\gamma = BB'/r+\Delta\theta, \tag{5}$$

where $\Delta\theta$ is the deviation of the same ray on refraction at the Bragg face. From Eq. (4)

$$\Delta\theta = \delta/\tan\theta, \tag{6}$$

hence

$$\delta = \frac{BB'}{r}\cdot\frac{\tan\beta}{1-\cot\theta\tan\beta}. \tag{7}$$

By means of this last formula the values of δ were calculated. Fig. 3, plotted as explained in connection with Fig. 1, is a sample of the results

from which BB' may be read off at once. It should be remembered that the slope of the lines is known from Eq. (1); it is not necessary to estimate their slope from the positions of the points. BB' was also calculated from each individual observed point of the sloping lines by means of Eq. (1). Of course the average of these calculations agrees closely with the graphical distance BB'. Table I contains a sample of such calculations, together with data on the measurement of plates for the Ca $K\alpha_1$ line. Fig. 3 is based on these measurements. The values of BB' in Table II are the mean of graphical values from plots like that of Fig. 3 and the average of the values calculated from the individual points as just explained.

The dispersion theory of x-rays, as developed by several writers[6, 7, 8] results in the following expression.

$$\frac{\delta}{\lambda^2}=\frac{e^2AZ\rho}{2\pi mc^2M}\left[1+\sum_k\frac{N_k}{N}\left(\frac{\lambda}{\lambda_k}\right)^2\ln\left\{1-\left(\frac{\lambda_k}{\lambda}\right)^2\right\}\right], \quad (8)$$

where A is Avogadro's number, Z the total number of electrons per molecule of the refracting medium, ρ the density, and M the molecular weight. N is the total number of electrons per cubic centimeter, while N_k is the number of electrons of kind k per cubic centimeter. On the short wave-length side of an absorption edge, where $\lambda<\lambda_k$, $\ln\{1-(\lambda_k/\lambda)^2\}$ in Eq. (8) should be replaced by $\ln\{(\lambda_k/\lambda)^2-1\}$. The values of δ/λ^2 are calculated from formula (8) and are compared with those from the observations. The comparison is made in Table II and in Fig. 4.

[6] R. de L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926).
[7] H. Kallman and H. Mark, Ann. d. Physik **82**, 585 (1927).
[8] J. A. Prins, Zeits. f. Physik **47**, 479 (1928).

Experimental Procedure

In using the Bragg method, in which the distance of the axis of the spectrograph from the

Table II. *Summary of results.*

Line	λ(X.U.)	Ref. line	BB' (mm)	Bragg face	Bevel face	$\delta/\lambda^2\times10^6$ Meas.	Calc.
Va $K\alpha_1$ Va $K\alpha_2$	2498 2502	Ni $K\alpha_1$ (2) Zn $K\beta_1$ (2)	0.123	(110)	(100)	6.4	6.9
Ti $K\alpha_1$ Ti $K\alpha_2$	2743 2747	Cu $K\beta_1$ (2)	0.135	(130)	(110)	7.0	6.8
"	"	S $K\alpha_1$ (1)	0.063	(110)	(100)	6.8	
Cs $L\alpha_1$	2886	Cu $K\beta_1$ (2)	0.215	(100)	(110)	6.8	6.7
"	"	" "	0.083	(130)	(110)	6.4	
Sc $K\alpha_1$ Sc $K\alpha_2$	3025 3028	Cu $K\alpha_1$ (2)	0.122	(100)	(110)	6.4	6.5
Sb $L\beta_1$	3218	Sn $L\beta_2$ (1)	0.543	(001)	(102)	5.5	6.2
Te $L\alpha_1$ "	3282 "	Cu $K\alpha_{1,2}$ (2) Ca $K\beta_1$ (1)	0.320	(001)	(102)	5.3	6.2
Ca $K\alpha_1$	3352	Ni $K\alpha_{1,2}$ (2)	0.280	(001)	(102)	5.3	6.1
Sn $L\beta_1$	3378	Ni $K\alpha_{1,2}$ (2) Ca $K\alpha_{1,2}$ (1)	0.229	(001)	(102)	6.0	6.0
Sb $L\alpha_1$	3432	Ni $K\alpha_{1,2}$ (2)	0.166	(001)	(102)	5.2	5.9
Sn $L\alpha_1$	3592	Co $K\alpha_{1,2}$ (2)	0.126	(001)	(102)	5.7	5.9
Ru $L\alpha_1$	4835	Cu $K\alpha_{1,2}$ (3)	0.572	(110)	(100)	4.5	3.8
Mo $L\beta_1$	5166	Ni $K\alpha_{1,2}$ (3)	0.274	(110)	(100)	4.9	4.6
S $K\alpha_1$	5361	Ti $K\alpha_{1,2}$ (2)	0.215	(110)	(100)	5.0	4.9
Mo $L\alpha_1$	5395	Cu $K\beta_1$ (4)	0.223	(110)	(100)	5.4	4.9

slit and from the photographic plate are equal, the position of a spectrum line remains fixed when the crystal, mounted with its face containing the axis of rotation, is turned to a new position. In this work the crystal was mounted so that both the Bragg and the bevel faces contained the axis of rotation. The line to be refracted and a convenient reference line were photographed together, both being reflected from the Bragg face. Several such photographs were taken, the crystal being moved about 1′ each time. Then several more photographs were taken with the reference line still reflected from the Bragg face, but the other line reflected from the bevel face. Different settings of the crystal were made here also. The method of locating the point D (Fig. 1) which gives the setting of the crystal for which the line whose refraction is to be studied is reflected at the line joining the two crystal faces, has already been described. This point was probably located to an accuracy of about 15 seconds.

The direction of the rays on striking the crystal was always in the sense shown in Fig. 2, and never in the opposite sense; for in the latter sense all rays of a certain wave-length would leave the crystal in almost exactly the same direction from both faces, and hence there would be practically no separation due to refraction.

When the rays leave the bevel face at a grazing angle less than one degree the absorption is very great and the refracted line is not sharp; hence most of the measurements were taken of lines of such a wave-length that the rays left the bevel face at an angle of from one to five degrees.

Results

In Table II are collected the complete results. The first column contains the symbol of the line whose index is to be found, the second its wave-length, the third the reference line. The numbers in parentheses in the third column indicate the order of the reference line. The fourth column contains BB' of Fig. 1 and Eq. (7). In column five are the Miller indices of the Bragg face, in column six those of the bevel face. The last two columns contain the values of δ/λ^2 calculated from formulas (7) and (8), respectively.

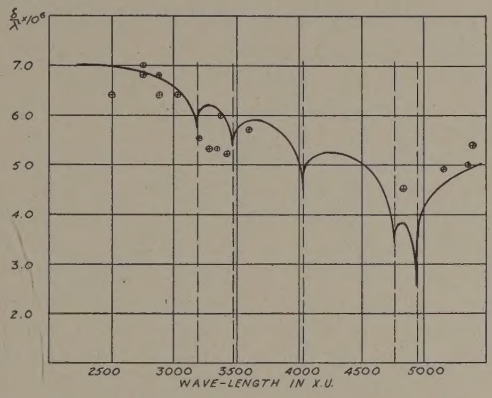

Fig. 4. Dispersion curve for x-rays in cerussite. The circles represent experimental values.

Discussion of Results

In Fig. 4 we have the curve for the value of δ/λ^2 for lead carbonate in the spectral region of the five M absorption edges of lead. The angles between the crystal faces were not suitable for measurements in the middle portion of the region, but the results indicate a falling value for δ/λ^2 as we approach M_{I} and M_{II}, then a rise again after M_{V} is passed. Only one good line could be found very near an edge. This was Sb $L\beta_1(\lambda = 3218)$ which is probably about 6 X.U. above M_{I} in wave-length. There was no evidence of any smaller value of δ/λ^2 for this particular line. However, in a substance with so many electrons per molecule as $PbCO_3$ one must approach very closely to the edge before there is any marked change in δ/λ^2. The point for Ru $L\alpha_1$ also fails to indicate the especially low value for δ/λ^2 to be expected in the narrow region between M_{IV} and M_{V}. The values of δ/λ^2 are probably accurate to some 10 percent. While the quantity undoubtedly shows a general diminution in value in the region of the M edges, it does not seem to decrease so much as required by Eq. (8), which results from the theory of anomalous dispersion.

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